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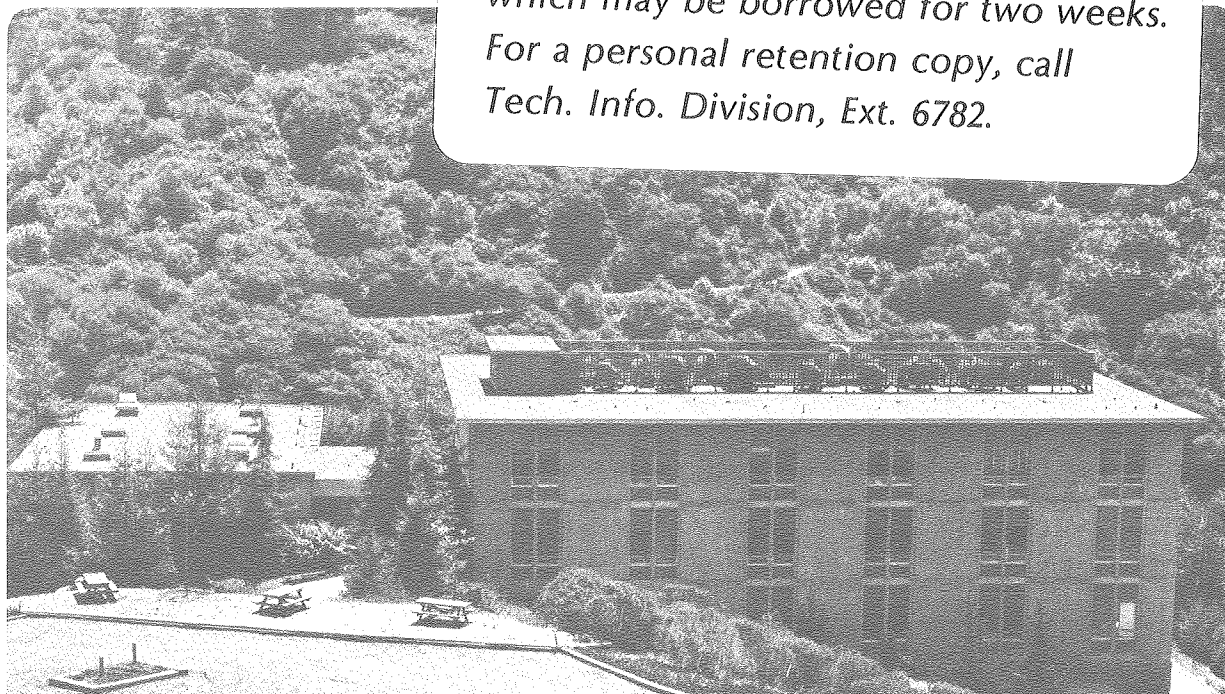
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A STEREOCHEMICAL TEST

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February 1981

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# The Nature of Sulfur Monoxide From Thiirane Oxide: A Stereochemical Test

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## Abstract

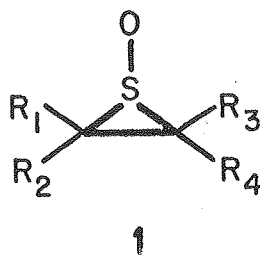
In order to study the stereochemistry of thiirane oxide decomposition, syn- and anti-2,3-dideuterothiirane-1-oxides and trans-2,3-dideutero-thiirane-1-oxide have been synthesized in three steps from cis- and trans-dideutero-ethylene via stereospecific formation of the corresponding oxiranes and thiiranes. The presence of the deuterium label was used so as not to perturb the course of the decomposition from that of the parent thiirane oxide.

Pyrolysis of the labeled thiirane oxides in both gas and solution phase proceeded with greater than 90% retention of stereochemistry. Analyses were performed by comparison of the infrared spectra of the product mixtures with standard calibrated samples. Attempts to trap possible biradical intermediates with di(p-anisyl)thio ketone gave a low yield of products possibly derived from addition to thiirane oxide. These results suggest a possible partial contribution of a biradical mechanism to the thiirane oxide decomposition. If bond rotation in the biradical is slow, this mechanism could be the sole mode of sulfur monoxide extrusion.

## Introduction

Among three membered ring compounds thiirane-1-oxides 1 are relatively unexplored. Nevertheless they constitute fascinating objects of study for

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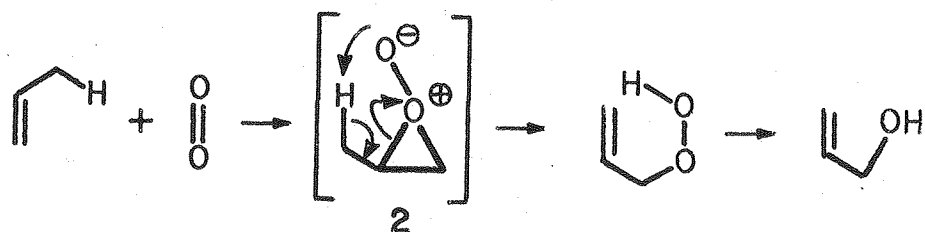
a variety of reasons. Thiirane oxides may be viewed as  $\pi$ -complexes of sulfur monoxide to ethylenes.<sup>1</sup> Indeed, their thermal decomposition furnishes alkenes and sulfur monoxide.<sup>2</sup> The latter is very reactive, producing as the final sulfur-containing products sulfur and sulfur dioxide.<sup>3</sup> The details of sulfur monoxide extrusion have been the subject of considerable recent discussion since both a concerted and a biradical (or dipolar) pathway present themselves as mechanistic alternatives. Related to this problem is the question of the nature and chemistry of the sulfur monoxide produced in this reaction. Much of the interest in sulfur monoxide is due to its role in the production of photochemical smog. One of the key steps in the production of sulfuric acid aerosols is the oxidation of sulfur dioxide to sulfur trioxide. The reaction of two molecules of sulfur dioxide to sulfur trioxide and sulfur monoxide has one of the highest rate constants ( $5400 \text{ ppm}^{-1} \text{ min}^{-1}$ ) of the possible atmospheric sulfur dioxide oxidation reactions.<sup>4</sup>

Sulfur monoxide is a sulfur analog of oxygen. Interestingly, the electronic states of sulfur and oxygen are quite similar, the ground state for both being the  $^3\Sigma^-$  state, with the singlets  $^1\Delta$  and  $^1\Sigma^+$ , respectively, constituting the first and second excited states.<sup>3,5,6</sup> (Table 1).

Table 1. Electronic States of Oxygen and Sulfur Monoxide

State of Molecule	Occupancy of highest orbitals	Energy relative to ground state (kcal mole <sup>-1</sup> ) (SO)	Energy relative to ground state (kcal mole <sup>-1</sup> ) (O <sub>2</sub> )
<sup>1</sup> Σ	$\uparrow \downarrow$	30	37
<sup>1</sup> Δ	$\uparrow \downarrow \_$	18.2	22
<sup>3</sup> Σ <sup>-</sup>	$\uparrow \uparrow$	0	0

The oxygen analog of thiirane oxide, the peroxirane 2, is the proposed likely intermediate in the reaction of singlet oxygen with alkenes possessing allylic hydrogens to give allylic hydroperoxides.<sup>7</sup>



The reaction of 2 has a direct analog in thiirane oxide chemistry (vide infra).<sup>8</sup> This reaction and some other unusual features associated with thiirane oxides has obscured mechanistic discussions dealing with the mode of their decomposition.

#### Thermal Decomposition of Thiirane Oxides: Previous Work

Since thiirane-1-oxide provides a convenient thermal source of sulfur monoxide, the nature of the latter becomes a subject of considerable interest. Should SO-dissociation proceed in a concerted (cheletropic) manner the principle of spin conservation would require the production

of both ethylene and sulfur monoxide in either the singlet or the triplet state. The measured activation enthalpy for the reaction (35 kcal/mole)<sup>2</sup> thermodynamically precludes the triplet-triplet possibility due to the high energy content of triplet ethylene. This leaves the formation of two singlets as the only viable concerted process. However, a thermochemical calculation makes this alternative also questionable. Lemal<sup>9</sup> has estimated the standard heat of reaction in the gas phase for thiirane oxide  $\rightarrow$  ethylene +  $^3\Sigma$  SO to be +21.5 kcal/mole. Considering the fact that  $^1\Delta$ SO lies 18.2 kcal/mole above the ground state triplet, one requires a minimum energy of 39.7 kcal/mole for production of  $^1\Delta$  SO in this process. Since the measured activation energy is 35 kcal mole<sup>-1</sup> the formation of singlet products appears thermodynamically unfeasible. On the other hand, the discrepancy is small and, given the assumptions made in calculating the standard heat of the reaction, and the fact that the measured activation parameters were obtained in solution, does not convincingly exclude a concerted pathway.

One of the more direct ways of gaining information about the identity of SO extruded from thiirane oxides is by spectroscopic means. Indeed, the decomposition products of thiirane oxide have been analyzed by both microwave<sup>10</sup> and EPR spectroscopy.<sup>11</sup> In both cases only triplet sulfur monoxide could be detected. However, a later kinetic study by EPR of the production and decay of  $^1\Delta$  SO (generated by the reaction of singlet oxygen with  $^3\Sigma^-$  SO) showed that the singlet sulfur monoxide species is heterogeneously deactivated with a very high efficiency by wall collisions in the reaction vessel.<sup>12</sup> The radiative lifetime for the singlet SO is less than 10<sup>-3</sup> seconds, several orders of magnitude less than that of singlet oxygen, for example. The authors calculated that ten per cent

of all wall collisions result in deactivation of the singlet sulfur monoxide to the triplet. It thus seems probable that, even if the decomposition of thiirane oxide produced singlet sulfur monoxide, it would be quenched to the ground, triplet state before it could be observed spectroscopically.

This finding may also be significant in an assessment of the conclusions drawn from the results of the reaction of sulfur monoxide (produced by the thermolysis of thiirane oxide) with stereochemically labelled dienes<sup>9,13</sup> and trienes.<sup>14,37</sup> The lack of stereoselectivity observed reactions suggested the intermediacy of ground state S0. However, as in the spectroscopic work, there is no unambiguous way of excluding its formation as a secondary product by fast collisional deactivation of an initially formed singlet species.

Another direct way of probing the viability of the various decomposition pathways of 1 under discussion relies on the observation of the stereochemistry in the carbon part of the molecule. Starting from thiirane oxides bearing a stereochemical label, one might expect that, if the decomposition were concerted, stereochemical integrity would maintain in the alkene product. Such a result might be indicative of the intervention of singlet S0. On the other hand, if the reaction proceeded through a diradical, scrambling of the stereochemical label should be observed if, after breaking the first carbon-sulfur bond, rotation occurred faster than loss of S0.

However, the interpretation of the results obtained from such experiments is not necessarily straightforward. For example, the expectation that stereoselective extrusion of S0 might be associated with its singlet state is based on the application of the empirical Skell criterion beyond

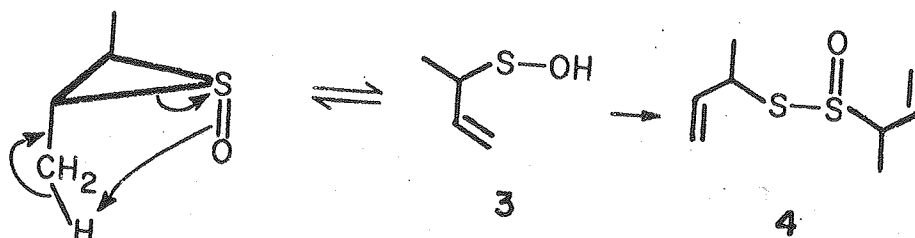
carbene chemistry.<sup>15</sup> This may not be warranted, particularly in the case of sulfur species. Thus, triplet sulfur adds to alkenes stereospecifically with retention<sup>16</sup> to produce thiiranes. The latter in turn eliminate sulfur with similar stereospecificity<sup>17</sup> by a mechanism which appears nonconcerted.<sup>18</sup> Thiirane-1,1-dioxides eliminate SO<sub>2</sub> also with retention, but the dependence of the rate of this reaction on solvent polarity indicates a dipolar intermediate.<sup>19</sup> Evidently, the second C-S bond to be broken is considerably weaker than the first and/or there are appreciable barriers to rotation in the intermediate ring-opened species.<sup>20</sup>

Another problem with stereochemical experiments is the label itself. It has to be chosen such as not to perturb the nature of the reacting species in any significant manner, nor to allow the occurrence of alternative pathways of decomposition. A case in point is the thermal chemistry of substituted thiirane oxides.

Hartzell and Paige<sup>21</sup> found that heating cis- and trans-dimethyl-1-thiirane oxide at 150°C in a g.c. injector port evolves SO and results in loss of stereochemical integrity in the alkene product. This was interpreted as suggestive of a mechanism in which sequential bond rupture through the intermediacy of a moderately rapidly rotating dipole would cause label scrambling. Subsequent work concerned with solvent effects led others to propose a biradical as the more likely initial product.<sup>13</sup>

Baldwin,<sup>8</sup> however, observed that the trans-isomer may undergo an intramolecular retro-ene reaction at ambient temperature involving the sulfoxide unit and a methyl hydrogen to produce the intermediate sulfenic acid 3





ultimately furnishing the thiosulfoxylate diastereomers 4. This process is general for thiirane oxides bearing suitably disposed alkyl groups.<sup>22</sup> Since sulfenic acid formation is reversible<sup>23</sup> and the reverse reaction may give both cis- and trans-labeled starting material, label scrambling might have occurred in the higher temperature gas phase work,<sup>21</sup> conditions that favor SO extrusion. Alternatively, the intermediate sulfenic acids might have decomposed by subsequent ene reactions directly to cis- and trans-alkenes and sulfur monoxide. Thus, it appears that the stereochemical results obtained in the decomposition of trans-1,2-dimethylthiirane oxide are of ambiguous origin. What about the cis-isomer?

cis-Dimethylthiirane oxide has been shown to adopt the anti-configuration with respect to the sulfoxide oxygen and the ring substituents. One might therefore suspect this molecule to be unable of entering the retro-ene label scrambling pathway mentioned for the trans-isomer. However, thietanoxide<sup>24</sup> and dialkyl sulfoxides<sup>25</sup> undergo ready thermal SO inversion. Should this occur in cis-dimethylthiirane oxide, a likely event at the elevated temperatures leading to SO extrusion, the retro-ene route would become available to the molecule.

Apart from the above possibilities both isomers might undergo a different type of isomerization reaction involving reversible opening of the carbon-carbon bond. Although this appears unlikely at first sight due to the estimated higher strength of this linkage, a relatively low energy concerted pathway might be available analogous to that observed in the isomerization of substituted cyclopropanes.<sup>26</sup> In conclusion, it

is clear that dimethylthiirane oxides are unsuitable substrates with which to determine the stereochemical outcome of SO departure.

In contrast to alkylsubstituted thiirane oxides, cis- and trans-diphenylthiirane oxides cannot undergo thermal retro-ene reactions. However, although the trans-compound eliminates SO almost completely stereospecifically (>98%), the cis-isomer gives close to equal amounts of cis- and trans-stilbene at low temperatures (>50°C) and nearly 90% trans-stilbene above 150°. <sup>27</sup> Similar thermal decomposition in the presence of di-para-anisylthioketone, an excellent carbon-radical scavenger, <sup>28</sup> gave a mixture of stereoisomeric trapping products. The formation of these adducts and the nonstereospecificity of the decomposition of cis-diphenylthiirane oxide strongly argue for the occurrence of a biradical decomposition mechanism. However, phenyl substitution might induce a strong perturbation on the decomposition chemistry of thiirane oxides, essentially masking the behavior of the parent molecule.

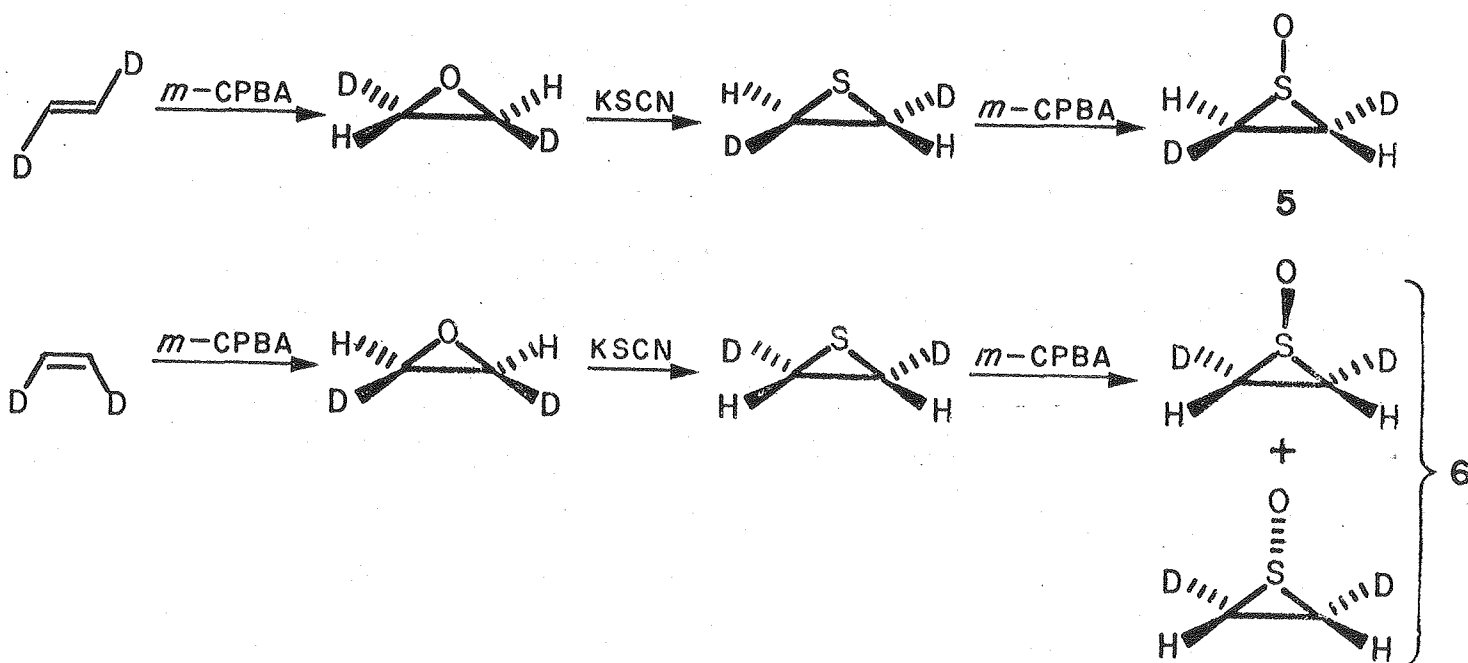
#### Synthesis and Decomposition of Deuterium-Labelled Thiirane Oxides

The above experiments appear to indicate that sulfur monoxide might be extruded from thiirane oxides with loss of stereochemistry in a stepwise manner. On the other hand its lower and higher oxidized analogs decompose with retention of stereochemical label. This unexpected discrepancy and our desire to clarify the nature of SO emerging in these processes led to our contribution to this problem outlined in this section.

In order to obtain unambiguous stereochemical information about the reaction we decided to employ a nonperturbing label on the thiirane nucleus: deuterium.

This required the synthesis of 2,3-cis- and trans-dideuterothiirane oxide 5 and 6. The cis- and trans-dideuteroethylenes required as starting materials were prepared using literature procedures starting from dideuteroacetylene.<sup>29</sup> An exhaustive study of the infrared bands of ethylene had identified diagnostic absorptions at 842 and 987  $\text{cm}^{-1}$  for cis- and trans-dideuteroethylene,<sup>30</sup> which could be used to verify the purity of the ethylenes and for the quantitative analysis of the ethylene produced in the decomposition of the labelled thiirane oxides.

A stereospecific synthesis of the starting dideuterated thiirane oxides is shown in the scheme:



The respective starting dideuterated ethylenes were stirred with a slight excess of purified<sup>31</sup> and sodium bicarbonate buffered m-chloroperbenzoic acid in benzene at room temperature for three days. After distillation of the resulting oxiranes they were exposed to a two-fold excess of potassium thiocyanate, known to stereospecifically (with double inversion) convert oxiranes to thiiranes.<sup>32</sup> After 24h the resulting thiiranes were vacuum distilled, dried, and oxidized at -20°C with m-chloroperbenzoic acid in CH<sub>2</sub>Cl<sub>2</sub>.<sup>22</sup> The benzoic acid was removed as the ammonium salt to allow the isolation of the thiirane oxides 5 and 6.<sup>33</sup> The deuterium-labelled thiirane oxides distilled at 40-41° and 1 mm pressure, in agreement with the reported values for unsubstituted thiirane-1-oxide.<sup>2</sup> Both had strong S=O and C-D stretches in the infrared spectrum and a parent peak of m/e 78 in the mass spectrum. The proton nmr spectra provided clear differentiation between 5 and 6. The mixture of the two cis-isomers 6 exhibited the expected two singlets, due to the pair of hydrogens located either syn or anti with respect to the oxygen on sulfur. The trans-isomer 5 gave a second-order AB pattern with much broadening due to deuterium coupling. A theoretical analysis<sup>34</sup> of the line pattern observed gave chemical shifts of 1.93 and 2.33 ppm for the two nonequivalent protons with a coupling constant of 10Hz.

Deuterium-decoupled 100 MHz proton nmr spectra were also determined using benzene-d<sub>6</sub> as solvent (see ref. 33). The spectrum of the trans-isomer showed the presence of a small amount (ca. 3%) of the cis-isomer. The presence of a small amount of the cis-dideuterothiirane oxide in the trans-compound is difficult to understand. Since an impurity of even 1% of

cis-dideuteroethylene in the starting trans-dideuteroethylene would have been detectable spectroscopically, the starting material could not have been the source of this problem. Moreover, since an identical sequence of reactions starting with cis-dideuteroethylene completely maintained stereochemical integrity en route to 6, it is unlikely that scrambling occurred due to nonstereospecificity in the reactions employed. It is possible that a small amount of a volatile impurity was generated in the synthesis of trans-dideuteroethylene which may have caused some loss of label at a later stage of the synthesis.

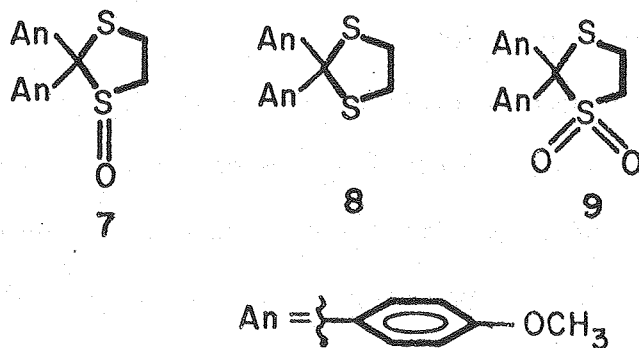
The composition of the ethylenic product obtained in the pyrolysis of the thiirane oxides was measured by comparing its gas-phase infrared spectrum run at several pressures with the spectra of a series of standard mixtures of cis- and trans-dideuterated ethylenes (98:2, 95:5, 90:10, 85:15, 75:25, 50:50). Several samples containing varying amounts of labelled thiirane oxide were pyrolyzed—both in 1,2,4-trichlorobenzene at 150°, and in the gas phase by vacuum transfer through a quartz tube heated to 350°C at 0.05 mm pressure.

In all cases the infrared spectrum of the ethylenic mixture obtained from the pyrolysis of cis-dideuterothiirane oxide indicated a cis:trans-dideuteroethylene ratio of 95:5. The trans-dideuterothiirane oxide (which contained 3% of the cis-isomer) produced a ratio of these products of 10:90. Considering the 3% presence of the cis-labelled impurity in starting material suggested 93% retention of stereochemistry. The maximum error in our measurements was estimated at ±2%. Thus, both of the above pyrolyses were at least 91% stereospecific.

Two experiments were performed to shed light on the source of the crossover product. In order to determine if the product sulfur monoxide

or some other by-product of the pyrolysis was a catalyst for the isomerization of the product ethylenes, sulfur monoxide was generated from unlabelled thiirane oxide in the presence of dideuterated ethylene. None of the isomerized ethylene was detected. Pyrolyses were also performed at lower temperature to allow some recovery of the starting material, which showed no scrambling of the label. This indicates that ring opening, rotation, and closure had not taken place nor had any species present catalyzed scrambling in the starting material.

To determine the possible presence of radicals in the decomposition of the unsubstituted thiirane oxides, attempts were made to trap any such radicals with di-para-anisylthioketone, a method used successfully on diphenylthiirane oxide.<sup>27</sup> Reaction of thiirane oxide did, however, not yield any of the adduct 7. Instead a small amount of 8 and 9 was formed. The proton nmr spectrum of the product mixture after initial chromatography



showed three methoxy singlets. Exhaustive column chromatography on silica led to separation of two products, one with one methoxy absorption in the nmr spectrum and a mass spectral parent ion at  $m/e$  318 consistent with

structure 8. Assignment was confirmed by Raney-nickel desulfurization to give dianisylmethane,<sup>35</sup> and by independent synthesis (thioketalization of dianisylketone). The assignment of structure 9 for the second product was in accord with its spectral data.

Sulfur monoxide generated from thiirane oxides in solution is known to reduce sulfoxides<sup>36</sup> and other oxides.<sup>37</sup> However, sulfur monoxide has not been known to oxidize sulfoxides. The formation of adducts 8 and 9 could be ascribed to the intermediacy of a ring-opened thiirane oxide biradical.

### Conclusions

Our experiments provide for the first time an unambiguous stereochemical test of the mode of decomposition of thiirane oxide. The data indicate extensive but not complete stereospecificity and suggest that these compounds are not unusual in their thermal behavior when compared with their higher and lower oxidized analogs. Similar modes of extrusion of the sulfur-containing moiety appear to take place. Of course, any scheme must account for the small amount of crossover in our experiment.

It is possible that both a stepwise biradical and a concerted mechanism are operating, the former being responsible for loss of stereochemical label. This biradical mechanism might indeed be the exclusive mode of decomposition, if rotation around the C-C bond of the biradical is relatively slow. The formation of an adduct with the radical scavenger also supports this contention: Thus, although all the currently available evidence points to the extrusion of ground state SO from thiirane oxides via a stepwise mechanism, ultimate proof is still lacking. It may have to await the design of unambiguous trapping or more sophisticated spectroscopic detection experiments.

## Experimental

Boiling points are uncorrected. Melting points were obtained on a Thomas-Hoover Unimelt apparatus and are uncorrected.  $^1\text{H}$  nmr spectra were recorded on a 60 MHz (Varian) spectrometer using  $\text{CDCl}_3$  as solvent unless otherwise indicated. Decoupling experiments were executed on a Hitachi Perkin-Elmer R-24B (60MHz) instrument. Chemical shifts are reported in ppm from internal tetramethylsilane. Routine IR spectra were run on a Perkin-Elmer 221 or 337 spectrophotometer and were calibrated using the  $1601\text{ cm}^{-1}$  absorption of polystyrene. Samples were prepared by evaporating solutions onto a KBr disc (unless mentioned otherwise). For infrared analysis of gases an apparatus was used which had a ball joint attachable to a vacuum line and stopcock leading into a cylindrical chamber of 10 cm length with a KBr disk at each end. To this cylinder a small side arm was attached which allowed condensation of gases. The quantitative IR work was done on a large drum Perkin-Elmer 421 spectrophotometer. Mass spectra and elemental analyses were provided by the Mass Spectral Services and the Microanalytical Laboratory of the University of California at Berkeley. Gas chromatography was performed on a Varian Aerograph Model 920 with a 20% UCW-98 on 80/100 mesh Chromosorb DMCS-AW, 0.25in.x10ft SS column unless otherwise noted. All chromatography was carried out on E.M. Reagents silica gel (70-230 mesh ASTM) and all preparative TLC on commercial silica gel plate (Merck) or on plates prepared with E.M. Reagents silica gel-PF 254 containing  $\text{CaSO}_4$  and fluorescent indicator. All solvents were purified by distillation from the appropriate drying agent, stored over 3A molecular sieves and vigorously degassed, when necessary, just prior to use. Impurities in nitrogen were removed by passage through a column of BASF catalyst R3-11 to remove oxygen and a column of 3A molecular sieves.



### Cis- and trans-2,3-Dideuterooxirane

meta-Chloroperoxybenzoic acid (10g, 58mmoles) was dissolved in benzene (150 ml) in a 1000ml round bottom flask also containing  $\text{NaHCO}_3$  (1g) and a magnetic stirrer on a vacuum line. The required deuterated ethylene (1l, 44.6mmoles) was introduced into an evacuated vacuum line to bring the manifold (and an empty 500ml flask) to a pressure of 725mm. The volume of the vacuum line had been determined to be 550ml. The 1000ml round-bottomed flask, which had previously been evacuated, was cooled to  $-196^\circ\text{C}$  and the stopcock opened to allow the ethylene to condense. The reaction was stirred for three days. Previous to this reaction a trial run was performed in a test-tube using unlabeled ethylene to ensure the formation of oxirane and to determine the time needed to allow the reaction to go to completion. The presence of oxirane was determined by the occurrence of an  $^1\text{H}$  signal at 2.75ppm (in benzene) (identical with authentic oxirane in benzene, lit. value 2.54ppm in  $\text{CCl}_4$ ).<sup>38</sup> Excess ethylene was removed under vacuum (freeze-thaw cycling) and the reaction product used immediately in the next step.

### Cis- and trans-2,3-Dideuterothiirane

A one liter flask containing water (100ml) and potassium thiocyanate (10g, 103mmole) was evacuated, cooled to  $-196^\circ\text{C}$ , and the requisite dideutero-oxirane in benzene added by vacuum transfer. The reaction mixture was stirred for 24h and the volatiles (including a little water) were subsequently vacuum transferred into a flask containing some sodium sulfate. A  $^1\text{H}$  nmr spectrum of the solution (1ml) using methylene chloride as a standard showed a singlet for the dideuterothiirane at 2.27ppm. Yield: 1.55g (56% based on ethylene).

### Cis- and trans-2,3-Dideuterothiirane Oxides 5 and 6

A solution containing dideuterothiirane (1.55g, 25mmoles) was added to methylene chloride (40ml) in a 100ml three-necked flask and cooled to 0°. Purified m-chloroperoxybenzoic acid (4.4g, 25.5mmoles) in methylene chloride (25ml) was added over 1 h in portions (5ml) and the reaction stirred for an additional hour. Ammonia was passed through the solution to precipitate the benzoic acid and the mixture purged with nitrogen, filtered, and the solvents removed under reduced pressure. The dideuterated thiirane oxides distilled at 40°-41° (1mm). Yield: 1.47g (74%). 5: m/e (rel intensity) 78(M<sup>+</sup>, 75%), 62(61%), 48(100%); IR(neat): 3010, 2950, 2280, 1060 cm<sup>-1</sup>; <sup>1</sup>H nmr: δ (CCl<sub>4</sub>) AB quartet, 2.33 and 1.93; (benzene-d<sub>6</sub>) 2.15 and 1.59. Anal.: Calc. for C<sub>2</sub>H<sub>2</sub>D<sub>2</sub>SO: C, 30.77; H, 7.69; S, 41.03. Found: C, 30.82; H, 7.78; S, 40.86. 6: m/e (rel intensity) 78(M<sup>+</sup>, 73%), 62(52%), 48(100%); IR(neat): 3020, 2960, 2260, 1050 cm<sup>-1</sup>; <sup>1</sup>H nmr: δ (CCl<sub>4</sub>) 2.33(s) and 1.93(s), (benzene d<sub>6</sub>) 2.15(s) and 1.59(s). Anal.: Calc. for C<sub>2</sub>H<sub>2</sub>D<sub>2</sub>SO: C, 30.77; H, 7.69; S, 41.03. Found: C, 30.70; H, 7.92; S, 40.91.

### Solution Phase Pyrolysis of cis- and trans-2,3-Dideuterothiirane Oxide

The thiirane oxide (410mg) was dissolved in 1,2,4-trichlorobenzene and heated to 150°C for 2 h. The gases were collected by vacuum transfer into an infrared gas cell and the IR spectrum recorded.

### Gas Phase Pyrolysis of cis- and trans-Dideuterothiirane Oxide

A standard flash vacuum pyrolysis apparatus was employed in this experiment. A sample reservoir containing 5 or 6 (50-150mg) was attached

to one end of a quartz tube heated by an oven at 350°C. The other end was connected to a cold trap (-196°C) leading to vacuum line at 0.05 mm pressure. The system was closed to the vacuum pump and the sample heated gently (50-60°C). The pyrolysate collected in the cold trap and was then transferred into an IR gas cell.

To determine the relative amounts of cis- and trans-dideuteroethylene in the pyrolysate known amounts of authentic material were mixed in varying proportions (98:2, 95:5, 90:10, 85:15, 75:25, 50:50, 25:75, 15:85, 10:90, 5:95, 2:98) and their IR spectra measured at varying pressures (200, 100, 50, 25, 12, 6 mm). The gases produced in the pyrolysis runs were collected and their IR spectra recorded at identical pressures. The series of spectra thus obtained was compared to the standards. The pyrolysis of cis-2,3-dideuterothiirane oxide gave spectra in best agreement with a 95:5 ratio of cis:trans deuteroethylene. The trans-2,3-dideuterothiirane oxide gave a 10:90 ratio of the same products.

#### Thermolysis of Thiirane Oxide in the Presence of trans-Ethylene-d<sub>2</sub>

Thiirane oxide (100mg, 1.25mmoles) was dissolved in 1,2,4-trichlorobenzene in a 500ml round-bottomed flask to which 100ml of trans-ethylene-d<sub>2</sub> had been added. Gases collected as described above and IR spectral analysis revealed the presence of trans-ethylene-d<sub>2</sub> and unlabelled ethylene but no cis-ethylene-d<sub>2</sub>.

#### Partial Pyrolysis of cis- and trans-Dideuterothiirane Oxide

A sample of labelled thiirane oxide (50mg, 0.625mmoles) was passed through a hot tube heated to 150° at 0.05mm pressure. The products were collected in a -196° cold trap. The gases were transferred into a gas cell, the liquid vacuum transferred into an NMR tube, and the

appropriate spectra recorded. The recovered thiirane oxide revealed stereochemical integrity.

Thermolysis of Unlabelled Thiirane Oxide in the Presence of Di-*para*-anisylthioketone.

Thiirane oxide (300mg, 3.8mmoles) was dissolved in toluene and the thioketone (5g, 19.4mmoles) added. The reaction was brought to reflux and heated for 24 hours. A silica gel column (250g) using 10% ether/pentane eluant separated excess thioketone from a yellow oil (200mg) collected in several fractions. The column chromatography was repeated on silica (100g) eluting with 5% ether/pentane. A light yellow solid (50mg) was obtained first, assigned structure 8, contaminated in later fractions with 9. 2,2-Bis(*p*-anisyl)-1,3-dithiolane 8: m.p. 80-81°C ( $C_6H_{12}$ ) (lit.<sup>39</sup> 81°-82°C); m/e (rel intensity) 318( $M^+$ , 8%), 290(18%), 258(64%), 135(100%); IR: 2950, 1480, 1440, 1250, 1175, 750, 740, 700  $cm^{-1}$ ;  $^1H$  nmr  $\delta$  ( $CCl_4$ ) 7.42(d,  $J=8.4Hz$ , 4H), 6.71(d,  $J=8.4Hz$ , 4H), 3.69(s, 6H), 3.24(s, 4H). Anal.: Calc. for  $C_{17}H_{18}O_2S_2$ : C, 64.15; H, 5.65; S, 20.12. Found: C, 64.21; H, 5.70; S, 20.06. The second compound could not be obtained completely pure and was assigned structure 9 (80mg): m/e 350( $M^+$ , 3%), 318(20%), 290(88%), 258(100%); IR: 2950, 1494, 1450, 1300, 1250, 1175, 1120, 700, 690  $cm^{-1}$ ;  $^1H$  nmr  $\delta$  ( $CCl_4$ ) 6.52-7.52(m, 8H), 3.70(s, 3H), 3.68(s, 3H), 2.65-3.06(m, 4H).

Desulfurization of 8.

Raney Nickel (1g) was treated with sodium hydroxide (2g) in water (25ml) at 75°. After one hour, the solution was decanted and the solid washed with water until neutral to pH paper. The water was decanted and replaced with ethanol (50ml). This material was transferred to a 100ml round-bottom flask and the dithiolane 8 (190mg, 0.59mmole)

added. After 6 h the solution was filtered and the solvent evaporated to give a light yellow solid. Recrystallization from cyclohexane gave white crystals of bis(p-anisyl)methane (100mg, 74%): m.p. 51°-52°; <sup>40</sup>m/e: 228 (M<sup>+</sup>, 100%), 197(72%), 121(37%); IR: 2950, 2900, 1620, 1460, 1260, 1200, 1120, 1040, 820 cm<sup>-1</sup>; <sup>1</sup>H nmr δ (CCl<sub>4</sub>) 7.03(d, J=9.4Hz, 4H), 6.70(d, J=9.4Hz, 4H), 3.77(s, 2H), 3.67(s, 6H).

#### Independent Synthesis of 8

Di(p-anisyl)ketone (lg, 4.1mmoles) was dissolved in acetic acid (25ml) at 100°C. To this solution was added ethanedithiol (2ml, 23.9 mmoles) and boron trifluoride etherate complex (2ml). The reaction mixture was stirred at reflux for 1 h, poured onto ice and neutralized with sodium carbonate. The solution was extracted three times with ether, washed with brine, and dried over magnesium sulfate. Solvent and excess ethanedithiol were removed under reduced pressure and the remaining solid recrystallized twice from cyclohexane, giving white crystals of 8 (1.08g, 83%): m.p. 81°-82°C.

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